Diagnostic criteria for hydrogen evolution mechanisms in electrochemical impedance spectroscopy

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ABSTRACT

Diagnostic criteria for hydrogen evolution reaction mechanisms in acidic and alkaline solutions, based on the dependence of equivalent circuit elements on the overvoltage and H^+ or OH^- ion concentration, are proposed. Determination of the kinetic parameters (rate constants and transfer coefficients) of hydrogen evolution reaction steps on the basis of the impedance data has been considered. Hydrogen evolution reaction on $CoSi_2$ electrode in acidic solutions is discussed using the proposed criteria, and it is shown that hydrogen evolution on cobalt silicide proceeds through the Volmer–Tafel–Heyrovsky mechanism.

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1. Introduction

Hydrogen evolution reaction (HER) is one of the most frequently studied electrochemical reactions. The interest in studying HER is due to the importance of this electrode process for theoretical electrochemistry as well as for hydrogen energy technologies, electrocatalysis, electrosynthesis, electrochemical corrosion, etc.

It is accepted that hydrogen evolution proceeds through the steps of discharge (Volmer reaction), electrochemical desorption (Heyrovsky reaction) and recombination (Tafel reaction) [1]. For acidic solutions, these steps are represented respectively by:

$$M + H^+ + e = MH_{ads} \tag{1}$$

$$MH_{ads} + H^+ + e = M + H_2 \tag{2}$$

$$MH_{ads} + MH_{ads} = 2M + H_2 \tag{3}$$

where M is the electrocatalyst. Elucidation of the HER mechanism and kinetics involves determination of the nature of steps which constitute the total process on the electrode, identification of the rate-determining step (rds) and also finding the values of the kinetic parameters.

For a long time such kinetic coefficients as $(\partial E/\partial \ln j)_{c_{H^+}}$, $(\partial E/\partial \ln c_{H^+})_j$, $(\partial \eta/\partial \ln c_{H^+})_j$, $(\partial \ln j/\partial \ln c_{H^+})_E$, $(\partial \ln j/\partial \ln c_{H^+})_\eta$, etc., obtained by direct current measurements, are used as criteria for HER mechanisms [2–4]. Here E is the electrode potential, j is the current density, η is the overvoltage ($\eta = E - E_{eq}$, E_{eq} is the equilibrium potential of the hydrogen electrode), c_{H^+} is the hydrogen ion concentration. Now, electrochemical impedance spectroscopy (EIS) becomes one of the most important tools for HER investigation [5–12]. That is why, it is necessary to have similar criteria for HER mechanism that are based on the impedance data analysis.

The theory of the Faradaic impedance of HER was developed in a number of works. Sufficiently full information about the structure of equivalent electrical circuits for electrodes on which HER takes place was presented by Harrington and Conway [7]. It was shown [7] that the Faradaic admittance, Y_F, for HER can be expressed in the form

$$Y_F = A + B/(i\omega + C) \tag{4}$$

where

$$A = F(\partial r_0/\partial E)_\theta \tag{5}$$

$(6)B = (F^2/q_1)(\partial r_0/\partial \theta)_E(\partial r_1/\partial E)_\theta; (7)C = -(F/q_1)(\partial r_1/\partial \theta)_E; r_0 = j/F$ is the net rate of charge transfer in HER; $r_1 = (q_1/F)(d\theta/dt)$ is the net rate of adsorbed hydrogen formation; θ is the electrode surface coverage by adsorbed atomic hydrogen; q_1 is the charge for H_{ads} monolayer formation; ω is the angular frequency of alternating current, $i = (-1)^{1/2}$.

Expression (4) can be put into correspondence with the equivalent electrical circuits shown in Fig. 1. In addition to the Faradaic impedance, these circuits contain the solution resistance R_s and electric double layer capacitance C_{dl}. At certain relations between

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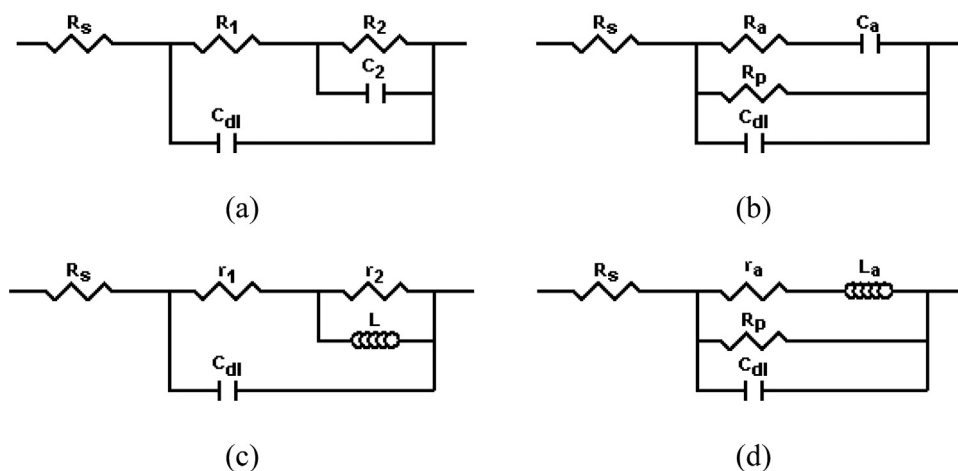*E-mail addresses:* kichigin@psu.ru (V.I. Kichigin), ashein@psu.ru (A.B. Shein).

Fig. 1. Equivalent electric circuits for an electrode on which hydrogen evolution reaction occurs [7].

elements all four of the equivalent circuits can provide exactly the same impedance spectra for all frequencies.

In accordance with Eq. (4), Faradaic impedance parameters for the equivalent circuit in Fig. 1(a) can be expressed as follows [7]:

$$R_1 = \frac{1}{A} \tag{8}$$

$$R_2 = -\frac{B}{A(AC + B)} \tag{9}$$

$$C_2 = -\frac{A^2}{B} \tag{10}$$

General expressions for the elements of other equivalent circuits (Fig. 1 (b-d)) are presented in Ref. [7]. Particular expressions will depend on the forms of the kinetic equations and adsorption isotherm.

In the present paper, a new approach to analysing the impedance of electrode, at which the HER proceeds, is proposed with the aim of elucidating reaction mechanism and determining the kinetic parameters of HER steps. The approach implies that straight line portions of experimental log$X$ vs. η curves (here X are the elements of the Faradaic impedance in equivalent circuit) are found, then the partial derivatives of log$X$ with respect to η and with respect to H$^+$ (or OH$^-$) ion concentration for these curve portions are determined, and they are compared with theoretically predicted values of the derivatives. The values of the rate constants are obtained from the intercepts of straight line portions of log$X$ vs. η curves. The analysis is performed for both Langmuir isotherm of hydrogen adsorption and Temkin isotherm (the latter is rarely used in HER impedance analysis). It is shown that study of the effect of H$^+$ (or OH$^-$) concentration on equivalent circuit elements can provide additional EIS criteria for HER mechanism; in previous studies, this issue was not discussed properly. At the end of the paper an example of the application of the proposed criteria for investigation of the HER on CoSi$_2$ in sulphuric acid solutions is presented.

2. Theoretical

When analysing the Faradaic impedance, the following assumptions were made. The kinetic equations for the steps (1) and (2) are written (Sections 2.1.1.1, 2.1.1.2, 2.1.2, 2.2.1.1, 2.2.1.2) assuming that the solution contains a significant amount of supporting electrolyte, i.e. double layer effects (Frumkin correction), when changing H$^+$ or OH$^-$ ion concentration, are not considered. The influence of hydrogen ions diffusion toward electrode, molecular hydrogen diffusion from electrode and atomic hydrogen absorption

by electrode material are not considered too. When analysing HER impedance, the equivalent circuit (a) in Fig. 1 will be used. The use of the circuit (b) will not affect the conclusions about HER mechanism and the results of determination of the kinetic parameters of HER steps.

2.1. Langmuir isotherm

When the Langmuir isotherm is fulfilled, the electrode surface is considered to be energetically homogeneous and the interaction between adsorbed hydrogen atoms is not taken into account.

2.1.1. Acidic solutions
2.1.1.1. Volmer–Heyrovsky mechanism. One can write for the Volmer–Heyrovsky mechanism:

$$-r_0 = k_1^o c_{H^+}(1-\theta)e^{-\alpha_1 FE/RT} - k_{-1}^o \theta e^{(1-\alpha_1)FE/RT}$$
$$+ k_2^o c_{H^+}\theta e^{-\alpha_2 FE/RT} - k_{-2}^o(1-\theta)e^{(1-\alpha_2)FE/RT} \tag{11}$$

where k_i^o are the rate constants for reactions in forward direction at E_{eq}, k_{-i}^o are the rate constants for backward reactions at E_{eq}, c_{H^+} is the hydrogen ion concentration at the electrode surface, E is the electrode potential measured with respect to the SHE, α_i is the transfer coefficient for ith step. The activity coefficients of ions are omitted from the rate equations, i.e. k's are the formal rate constants.

By going from potentials to overvoltages the expression for r_0 becomes:

$$-r_0 = k_1 c_{H^+}^{1-\alpha_1}(1-\theta) - k_{-1}c_{H^+}^{1-\alpha_1}\theta + k_2 c_{H^+}^{1-\alpha_2}\theta - k_{-2}c_{H^+}^{1-\alpha_2}(1-\theta) \tag{12}$$

where

$$k_i = k_i^o \exp(-\alpha_i F\eta/RT) \tag{13}$$

$$k_{-i} = k_{-i}^o \exp((1-\alpha_i)F\eta/RT) \tag{14}$$

Similarly, for r_1 one obtains the expression:

$$-r_1 = k_1 c_{H^+}^{1-\alpha_1}(1-\theta) - k_{-1}c_{H^+}^{1-\alpha_1}\theta - k_2 c_{H^+}^{1-\alpha_2}\theta + k_{-2}c_{H^+}^{1-\alpha_2}(1-\theta) \tag{15}$$

The powers $(1 - \alpha_i)$ on the H$^+$ concentration in Eqs. (12) and (15) result from insertion of $E = \eta + E_{eq}$ and $E_{eq} \approx (RT/F)\ln c_{H^+}$ into (11). In the following, we consider the impedance parameters as functions of overvoltage. Also we assume that the transfer